Combustion Research Facility News

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New Thermodynamic Model Enables Predictions of Corrosion in Glass Furnaces

A new model has been used to predict heats of formation, entropies, and heat capacities of the liquid product that forms when alkali hydroxides such as NaOH and KOH react with silica-based refractory brick used in the ceilings or "crowns" of glass-melting furnaces (Figure 1). Because of the nonideal behavior of these product liquids, special methods are required to obtain thermodynamic parameters. Funded by the DOE Office of Industrial Technologies, in collaboration with a consortium of three glass companies, three gas suppliers, and two refractory manufacturers, Mark Allendorf and Professor Karl Spear of the Pennsylvania State University modeled existing data and extracted thermodynamic properties.

Refractory brick composed primarily of silica is commonly used to line the interiors of glass-melting furnaces. In air-fired furnaces, the crown typically lasts about 10 years. However, when air was replaced with pure oxygen in many melting furnaces, the increased production of alkali hydroxides led to substantially higher silica corrosion rates. Typical penetration of refractory by alkali hydroxides is depicted in the micrographs shown in Figure 2. In some cases, crown lifetimes decreased by as much as twofold. The high cost of rebuilding these furnaces is driving organized efforts to either reduce corrosion to acceptable rates, or identify alternative refractory materials. Since silica brick is an attractive material because of its low density (which simplifies furnace construction), low thermal conductivity, and low cost, reducing corrosion is preferred to using more corrosion resistant, but also more costly, refractories.

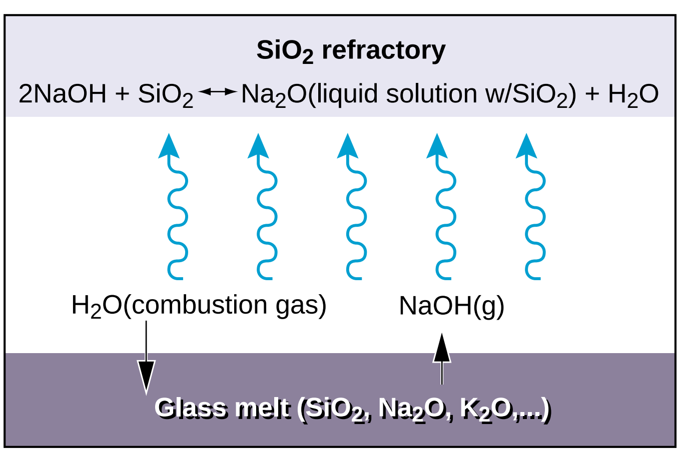

Figure 1. Schematic of the processes involved in the corrosion of crown glass in melting furnaces. NaOH produced from the reaction of the combustion gas with the glass melt reacts with SiO_2 in the crown of the furnace to produce Na_2O.

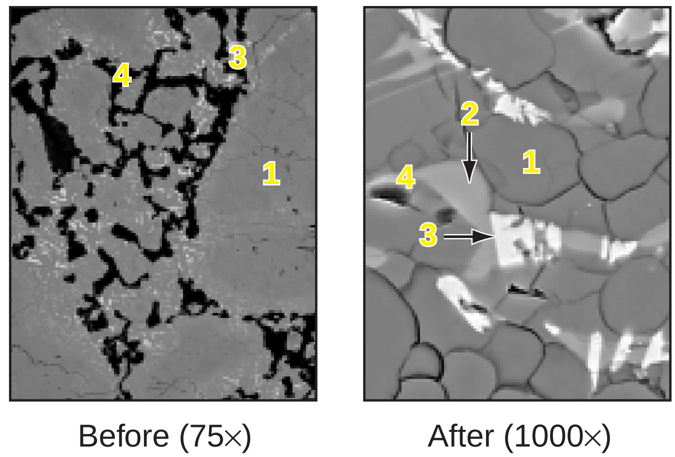

Figure 2. Micrographs of crown glass before and after alkali hydroxide corrosion. The dark gray areas (1) are silica grains, the light gray areas (2) glassy sodium silicate, the white areas (3) calcium silicate, and the black areas (4) voids.

The new thermodynamic data were used in equilibrium calculations to predict the regimes in which corrosion is thermodynamically possible. The curve in Figure 3 shows that for a given gas-phase partial pressure of NaOH, silica refractory should only corrode (i.e., form a liquid sodium silicate phase) in the region of conditions to the right of the curve. For example, if the NaOH partial pressure is higher than that in equilibrium with crystalline silica and the liquid sodium silicate phase (represented by the curve in Figure 3), then corrosion can occur. The lower branch of the curve thus defines a "critical temperature," above which corrosion does not occur for a given partial pressure. Above the lower branch of the curve, corrosion will not occur because the partial pressure of NaOH is less than the equilibrium value.

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Corrosion *(continued from previous page)*

These results are consistent with observations in actual furnaces, which show that insulating the cold side of the crown refractory, and thus increasing the temperature of the hot face, slows the rate of corrosion. Interestingly, the results also suggest that, at high temperatures (i.e., above the upper branch of the curves), corrosion should resume, since the NaOH concentration will again exceed the equilibrium value. At NaOH concentrations above about 125 ppm, corrosion can occur at all temperatures because the partial pressure of NaOH is always above the liquid-SiO_2 (crystalline) equilibrium value.

Current efforts are devoted to obtaining comparable data for corrosion of alumina-based ceramics and assessing the effects of calcium oxide, which is a component of many silica-based refractories.

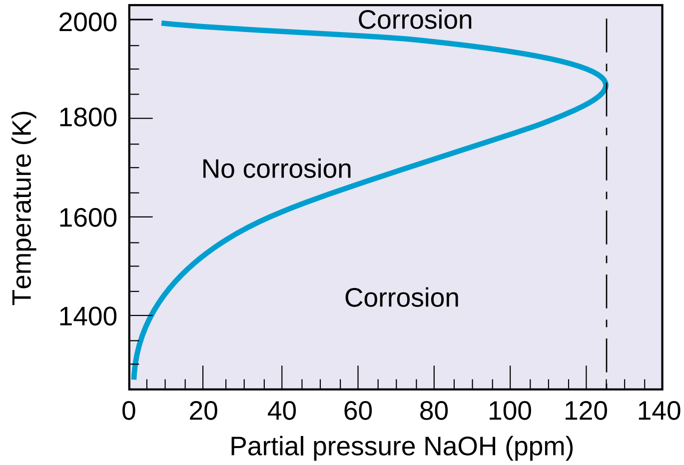


Figure 3. Zones of corrosion as a function of gas-phase partial pressure of NaOH for air and oxygen-fired glass melting conditions. Since the curve represents the liquid sodium silicate phase, corrosion can only occur when the partial pressure of NaOH is on the right side of the curve.

People



Post-doctoral associates Brian Higgins (l), Uta Goers (c), and Fabio DiTeodoro (r) have recently left the CRF for new positions. Brian, who worked with Dennis Siebers for 3 years in the Diesel Simulation Facility, accepted a faculty position at Cal Poly, San Luis Obispo. Uta worked with Tom Kulp on gas imaging in the Remote Sensing Laboratory for 3 years. She joins Corning Inc. in Corning, New York to develop optical components for telecommunications. Fabio will work at the Naval Research Laboratory in Washington DC, on fiber laser amplifiers. During his stay at the CRF, Fabio studied CO detection by two-photon fluorescence in Roger Farrow's lab.


Greg Fiechtner and Linda Blevins are new additions to the CRF staff. Linda comes to the CRF from NIST where she was a principal investigator in the Fire Science Division. Linda will study coal and biomass combustion and continue a SERDP study of soot generation that she started at NIST. The CRF also welcomes back Greg Fiechtner, who was a postdoctoral associate in Rob Barlow's lab during 1994–6. Greg returns as a staff member in the Engine Combustion Department as the principal investigator in one of our gasoline direct-injection engine laboratories.

Dave French, whose artwork graced most CRF publications, presentations, and posters for over 10 years, passed away suddenly in August. Dave was a talented all-around artist, but he had a special gift for portraying complicated experimental equipment in easily understandable drawings. His friends and colleagues miss him.

Experiments and Modeling Establish Fundamental Kinetics of New Ethane Dehydrogenation Process

A Sandia team comprising Mark Allendorf, Russ Hanush, Tony McDaniel, and Steve Rice has worked closely with Dave Zerkle at Los Alamos National Laboratory to develop a combined reduced

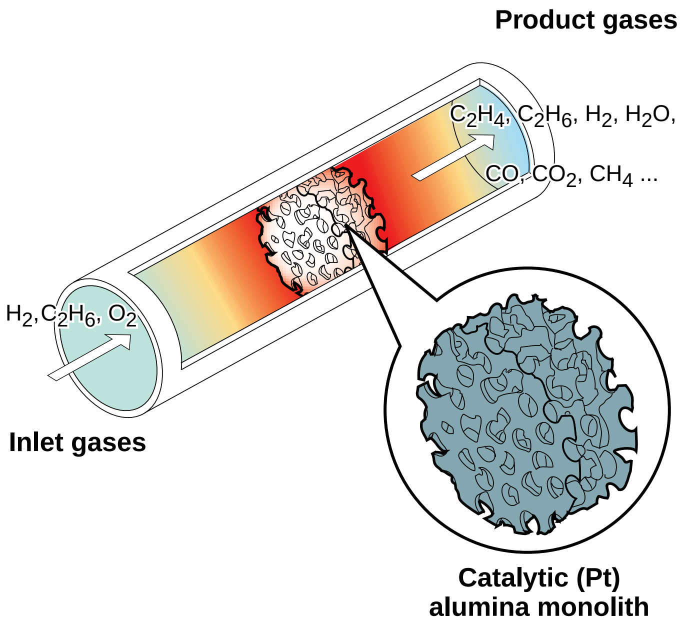


Figure 1. Short-residence-time reactor for the catalytic oxidative dehydrogenation of ethane to ethylene. Typical feed conditions are ethane, hydrogen, and oxygen at a mole ratio of 2:2:1 at ambient temperature and a few atmospheres pressure. The catalytic monolith is maintained at approximately 1000°C by heat released from the oxidation of hydrogen by oxygen co-fed with ethane.

gas-phase and catalytic-surface elementary reaction mechanism for a new catalytic process for the dehydrogenation of ethane to ethylene. Ethylene production is the biggest user of energy in the U.S. chemical industry, consuming more than 400 trillion BTUs for heat and power and 1010 trillion BTUs as feedstock. The new method, demonstrated several years ago by Professor Lanny Schmidt and coworkers at the University of Minnesota, uses a catalytic short-contact-time reactor (see Figure 1) and has the potential to significantly reduce energy consumption. The project is part of the U.S. Department of Energy's Office of Industrial Technologies, Industries of the Future Program.

The mechanism has been successfully incorporated into a two-dimensional computational fluid-dynamics code to simulate conversion, selectivity, and thermal properties of a single pore in the catalytic monolith. Modeling results suggest that both simultaneous heterogeneous surface reactions and homogeneous high-temperature gas-phase pyrolysis produce significant amounts of ethylene. The selectivity for ethylene and the ethane conversion efficiency both depend on the competition between these reaction pathways.

Experiments at Sandia examined the competition between hydrogen and hydrocarbons for oxidation sites on the platinum catalyst. A low-pressure high-temperature stagnation flow reactor was used to explore high temperature catalytic activity of polycrystalline platinum in an idealized geometry that lent itself to facile computational simulation. The reactor can be used to spectroscopically probe the composition of the reactant mixture in the immediate vicinity of the externally heated catalyst. Alternatively, formation of reaction products and the consumption of oxygen as the fuel feed composition is varied can be measured using downstream mass spectrometric analysis of the gas composition.

Measurements of water formation and oxygen consumption in the presence of varying amounts of methane and ethane at temperatures below the reactor autothermal point showed significant differences in what the mechanism predicts and what the experimental results show for the reactivity of the two hydrocarbons. There was also evidence for long-term catalyst deactivation (see Figure 2). Water formation and cooling of the catalytic substrate when ethane is added to a 4:1 mixture of hydrogen and oxygen, illustrates that ethane can effectively reduce the otherwise high catalytic activity of platinum for the formation of water.

These experiments suggest that although the elementary mechanism can represent many aspects of ethylene production, a predictive model will require a more refined treatment of surface reactivity or sticking efficiency of light hydrocarbons on platinum.

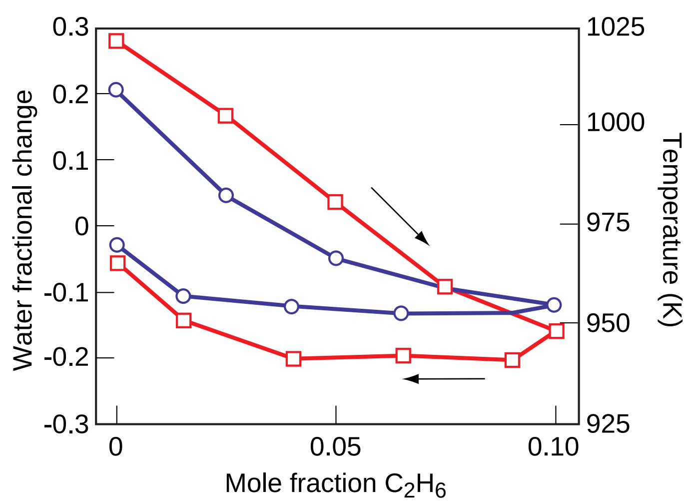


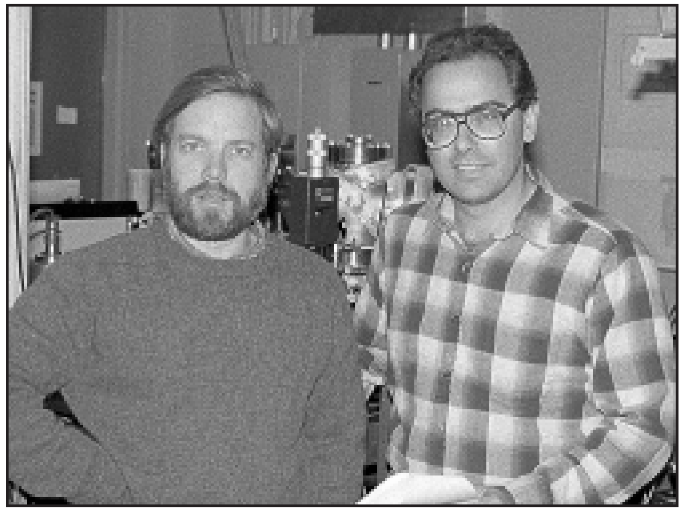
Figure 2. Exposure to ethane, of the order of 10 minutes for each data point, deactivates the catalyst surface. Both the autothermal surface temperature (red line) and the rate of H_2O formation (blue line) show that the surface is much less reactive after ethane exposure. Going in the reverse direction (from a mole fraction of 0.10 to 0.00), the autothermal surface temperature and H_2O formation rate do not return to their initial values, pointing to a loss of catalytic activity over time.

Awards

Chandler and Houston Win American Physical Society's Broida Prize

The 2001 American Physical Society's Herbert P. Broida Prize has been awarded to David W. Chandler, Sandia National Laboratories, and Paul L. Houston, Cornell University, "for their critical contributions to the investigation of vibrationally and rotationally resolved molecular photodissociation and reaction dynamics, in particular, for the invention and development of the photofragment ion-imaging method." The ion-imaging approach takes advantage of electronic imaging technology to observe the dynamics of photodissociation processes with a degree of detail unmatched by any other method.

The Broida Prize was established in 1979 as a memorial to and in recognition of the accomplishments of Herbert P. Broida, late Professor of Physics at the University of California, Santa Barbara. It is awarded to recognize an outstanding contribution to the field of atomic and molecular spectroscopy or chemical physics. Previous recipients include Nobel Laureates Steven Chu and Ahmed Zewail.



Broida Prize winners, Cornell Professor Paul Houston (l) and Dave Chandler, photographed in 1986 at the close of Professor Houston's visit to Dave's laboratory. During the visit, they demonstrated a new technique for determining the velocity distribution of photodissociation fragments. Since that time, the technique, ion imaging, has been adopted by laboratories throughout the world.

Tunable Infrared Spectrometer wins SERDP Project of the Year Award

The DoD/DOE/EPA Strategic Environmental Research and Development Program (SERDP) chose Sandia's project, "Development of a Novel Laser-Based Spectrometer for Measurement and Monitoring of Organic Emissions", as one of their top projects for FY99, and the winner in the compliance category. Scott Bisson, the project's principal investigator, was formally recognized on November 28, 2000 as one of the "outstanding researchers" in the compliance thrust area.

The award-winning spectrometer, which couples a broadly tunable laser source based on periodically poled lithium niobate (PPLN) with photoacoustic spectroscopy, enables the accurate detection of small amounts of volatile organic compounds.

Events

CHEMKIN Workshop

The second biennial workshop on CHEMKIN, held in Edinburgh, Scotland on July 30 prior to the start of the 28th International Symposium on Combustion attracted over 200 participants. Over the years, CHEMKIN has not only enabled significant strides in the modeling of combustion, but has become an important educational tool. Workshop participants discussed ideas on how to advance the computational modeling of chemical systems and expand the application of these approaches in combustion-related research and education. The workshop was co-sponsored by Sandia, the USDOE, and Reaction Design.

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Director: William J. McLean
Mail Stop 9054

Editor: Howard Lentzner
Email: hllentz@sandia.gov
Designer: Norma Calderon-Zablocki

Spectroscopic Study of Low-Pressure Dimethyl Ether Flames Confirms Most Predictions of Kinetic Model

Dimethyl ether (DME) has been proposed as an alternative diesel fuel that may meet requirements for simultaneous low NO_x and low particulate emission. DME has a high hydrogen-to-carbon ratio and no carbon-carbon bonds, features that should reduce particulate emission. Recent engine tests have confirmed that DME can reduce emissions from real engines. Furthermore, the addition of DME to methanol-fueled diesel engines has been demonstrated to enhance ignition and significantly reduce emission of unburned hydrocarbons.

Andrew McIlroy, Toby Hain, Hope Michelsen, and Professor Terrill A. Cool of Cornell University have studied the structures of low-pressure DME/oxygen/argon flames. Molecular beam sampling mass spectrometer (MBMS) methods and laser-induced fluorescence (LIF) were used to probe the chemistry of these flames. Shown in Figure 1, the apparatus includes both an electron-impact ionization quadrupole mass spectrometer (EI-QMS) and a single-photon vacuum ultraviolet (VUV) photoionization time-of-flight (PI-TOF) mass spectrometer (MS).

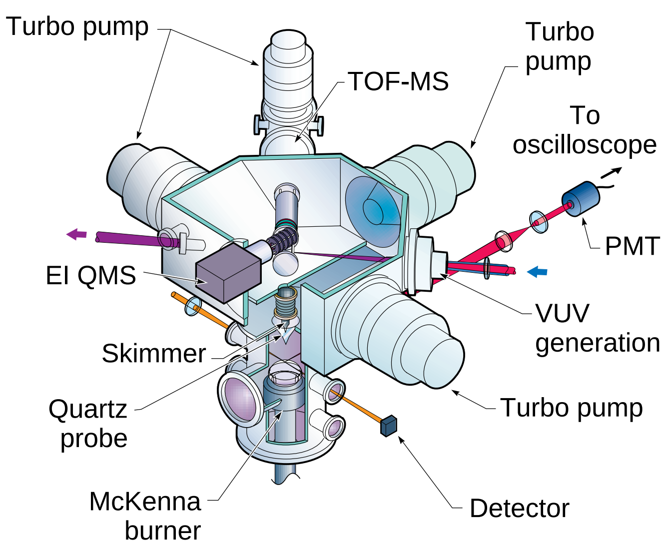


Figure 1. Schematic of the low-pressure flame, molecular beam sampling mass spectrometer showing the time-of-flight and quadrupole mass spectrometers and the laser setup for LIF detection of OH.

Experimental results were compared to the predictions of the detailed chemical kinetic model of H. J. Curran at Lawrence Livermore National Laboratory and S. L. Fisher and F. L. Dryer at Princeton University. As shown in Figure 2a, the model of Curran et al. does well at reproducing the major stable species: DME, O_2, CO, CO_2, H_2O, and H_2. Somewhat more H_2 than predicted is produced, particularly in the rich flame. The production of minor species (formaldehyde, OH, CH_4, and acetylene) agrees fairly well with the model as shown in Figure 2b. The shape and magnitude of the formaldehyde peak are

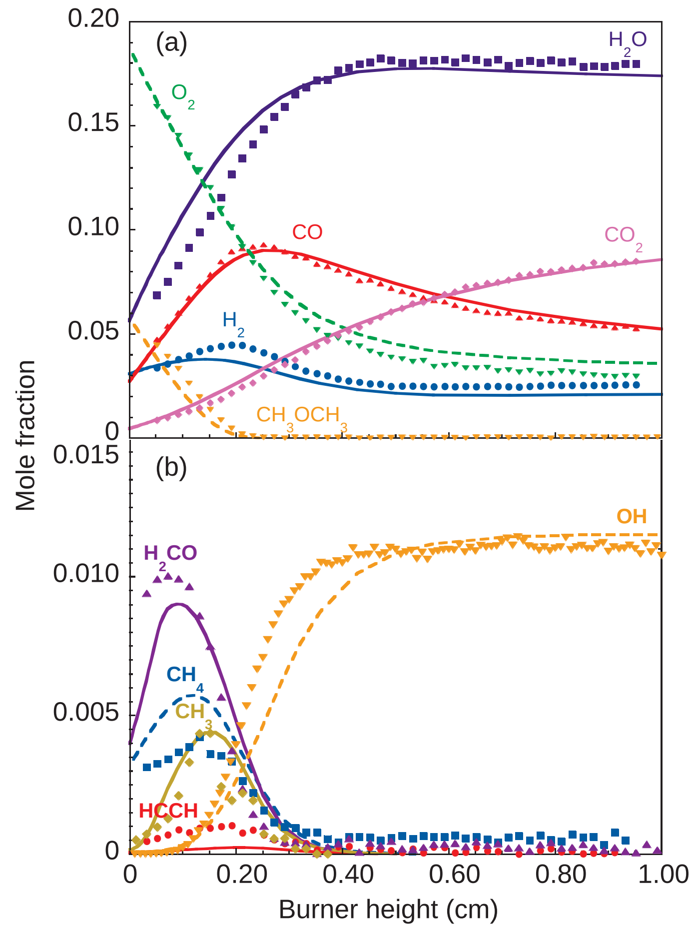


Figure 2. Measured (symbols) and calculated (lines) species mole fractions for a dimethyl ether/oxygen/argon flame of stoichiometry 0.98 as a function of height above burner at 30.0 torr. a) Major species mole fractions measured by MBMS with EI-QMS. b) Minor stable species measured by EI-QMS, OH measured by absorption-calibrated LIF, and CH_3 measured by PI-TOF-MS.

well reproduced within the accuracy of the calibration data, ~10%. The experimental methane mole-fraction profile peaks further from the burner and displays a different shape than the model predicts. The model also over predicts the methane mole fraction. The predicted and measured acetylene profile shapes are in good agreement, but the magnitude of the experimental data is significantly higher than that predicted.

The experimental disappearance of DME is well reproduced by the model. The primary mechanisms for DME removal are hydrogen abstraction to form CH_3OCH_2 and thermal decomposition to form methyl and methoxy radicals. Since the primary loss of CH_3OCH_2 is through decomposition to form methyl and formaldehyde, the correct prediction of DME loss should be a good indicator of methyl formation. Figure 2b shows the relative experimental methyl profile for a near stoichiometric flame, which agrees well with the model in shape and

(continued on next page see Spectroscopic Study)

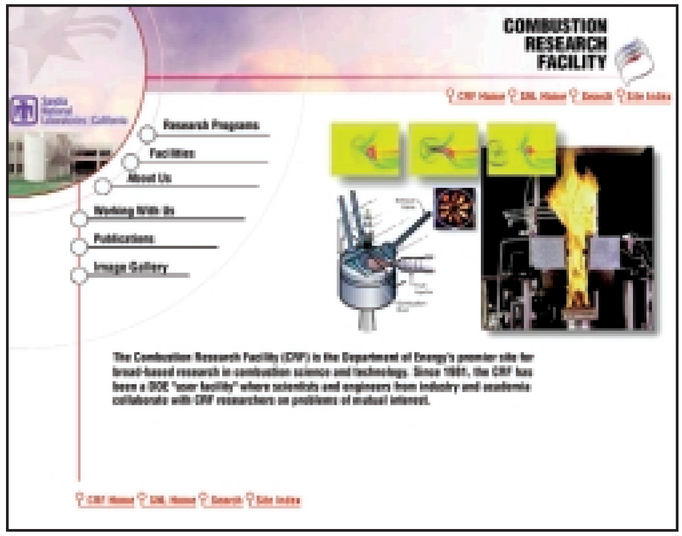
Spectroscopic Study *(continued from previous page)*

position. However, studies at other stoichiometries show less methyl in richer flames where the model predicts higher concentrations.

The model predicts that the predominant methyl loss reactions in low-pressure flames produce formaldehyde and methane. The experimental formaldehyde profiles are well reproduced by the model. Somewhat larger discrepancies are noted for methane, particularly in the rich flame. Since fuel-rich flames will certainly produce more methyl, it is most likely that the discrepancy between the model and experiment is due to unaccounted-for methyl loss channels that are specific to rich flames.

Redesigned CRF Website Now Online

On November 1, the CRF went public with its new redesigned website. Besides the new graphic design and up-to-date descriptions of research and facilities, the site has job postings, a searchable gallery of images that includes the photographs and drawings that have and will appear in CRF publications, a bibliography of the last three years of articles published in the refereed literature by CRF staff, and the capability to search for old articles from the CRF News. While several sections of the site are still being rebuilt, readers are urged to try the new site at http://www.ca.sandia.gov/CRF/ and direct their comments and suggestions to Webmaster Taz Bramlette.



Job Openings at the CRF

The CRF has a number of openings for career, limited-term, and postdoctoral positions at the CRF. Mechanical engineers, computer scientists, chemists, physicists, and technologists are encouraged to find out more about these positions by looking at the job descriptions on the CRF website (http://www.ca.sandia.gov/CRF/jobs.html) or the Sandia Corporate website (http://www.sandia.gov/Employ/emphome.htm).

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Sandia National Laboratories
Mail Stop 9056
P.O. Box 969
Livermore, California 94551-0969

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